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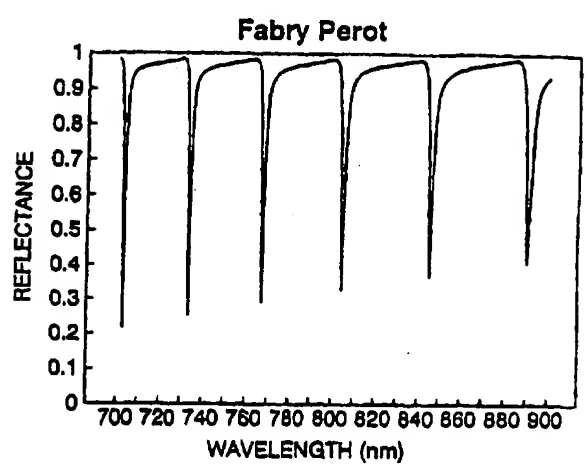
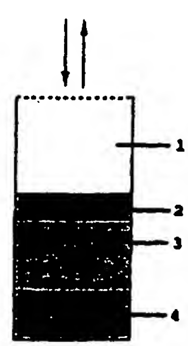
(54) Title: DIGITAL STORAGE MEDIUM BASED ON FABRY-PEROT PRINCIPLE

(57) Abstract

The present invention is in the field of digital storage media, more particularly on so-called WORM media (write-once-read-many-times compact discs) and rewritable media. The digital storage medium according to the invention comprises a grooved substrate (1) provided with a thin reflective layer (2) being partially transparent, which is provided with a layer (3), which comprises liquid crystalline material having a thickness (d) between 100 and 1200 nm, which is provided with a thick reflective layer (4) having a reflectance above 50 %. When using a CD according to this invention, the Fabry-Perot phenomenon is used to obtain or enhance a difference in reflection between the written and unwritten state.





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DIGITAL STORAGE MEDIUM BASED ON FABRY-PEROT PRINCIPLE

The present invention is in the field of digital storage media, such as compact discs (CDs) and digital tapes or cards, more particularly on so-called WORM media (write-once-read-many-times compact discs or tapes) and rewritable CDs and tapes. These types of media allow the information being written by the consumer.

In conventional read-only CDs the information is stored in pits which are embossed in the disc. The reading is based on pit-edge interference: As the laser focus is wider than the pit (0.6 μm), interference occurs between the laser light which falls within the pit and laser light which falls outside the pit (land). This results in a modulation in reflection, which is used for reading the information.
The conventional read-only CDs are only suitable for large production, as the production steps (for obtaining a written disc) are rather complicated and therefore only cost effective in mass production. There is a need for CDs and digital tapes or cards which can be produced in small quantities, or which can even be written by the consumer himself. One of the proposed concepts for this kind of WORM or rewritable CD is a CD comprising a liquid crystalline polymer (LCP) layer which is coated on a reflective layer. The writing is done by locally changing the phase of the LCP by means of laser irradiation. This results in a change of refractive index in the pit. The reading is again based on pit-edge interference: When irradiating with the reading laser the light travels through the LCP layer and reflects at the reflective layer. As the refractive index within a pit differs from the refractive index outside the pit (land), the optical pathlenght within the pit differs from that of the land. The laser light which falls within the the pit interferes with the light which falls on the land. The resulting reflection modulation is used for reading the information. This kind of CD is described in, for instance, CA-A1-2,014,698.

In EP-A1-0 608 924 a storage medium is described which comprises a homeotropically aligned LCP layer having a dichroic dye dispersed therein. The reading principle is now based on difference in absorption: In the homeotropic phase the dichroic dye is alligned along with the mesogenic groups of the LCP, which is perpendicular to the surface of the medium. In this state there is only low absorption of the incident light by the dichroic dye molecules, thus a high reflectance. After local irradiation of the LCP, the mesogenic groups, and thus the dye molecules, are orientated randomly, which results in a higher absorption of the incident light by the dye molecules, thus a lower reflectance.

There is still need of improvement in reflectivity and contrast in the WORM media and rewritable media proposed sofar.
The present invention provides a digital medium having an enhanced change in reflection.

The digital storage medium according to the invention comprises a grooved substrate (1) provided with a thin reflective layer (2) being partially transparant, which is provided with a layer (3), which comprises liquid crystalline material having a thickness (d) between 100 and 1200 nm, which is provided with a thick reflective layer (4) having a reflectance above 50%.

Thus, in comparison with the known digital storage media, an extra thin reflective layer is present, resulting in the liquid crystalline material layer (3) being sandwiched between two reflective layers. Herewith a Fabry-Perot etalon is created. The Fabry-Perot phenomenon is used to obtain a difference in reflection between the written and unwritten state in the digital storage medium. The difference in reflection between the written and unwritten areas in digital media based on difference in absorption and digital media based on pit-edge interference may also be enhanced by introducing the Fabry-Perot

phenomenon. A Fabry-Perot etalon typically consists of two parallel, reflecting layers that are placed at some distance (d) from each other. The dependence of the reflectance of a Fabry-Perot etalon on the wavelength is shown in figure 1, wherein schematically a CD is depicted with a substrate (1) having a refractive index of 1.58 and a thickness of 1.2 mm, a thin reflective layer (2) having a refractive index of 0.08 + i 4.60 and a thickness of 30 nm, a liquid crystallina material layer (3) having a refractive index of 1.67 and a thickness of 5 μm, and a thick reflective layer (4) having a refractive index of 0.08 + i 4.60 and a thickness of 200 nm. In general, the reflectance is high. At regular intervals, however, the reflectance changes abruptly to a low value. This negative peak in reflectance is hereinafter referred to as reflection dip. This resonance-like behaviour occurs when light cycling back and forth between mirrors interferes constructively with itself. This is the case when the requirements of equation 1 are fulfilled. If the requirements of equation 1 are fulfilled the reflectance is low.

$$\Phi + (4\pi \times n \times d)/\lambda = m \times 2\pi \qquad \text{[equation 1]}$$

wherein Φ stands for the phase shift of the laser light on reflection by the mirrors,

n stands for either n_u or n_w,

d stands for the layer thickness of the liquid crystalline material,

λ stands for the wavelength of the laser light used for reading,

m is an integer from 1-5.

The phase shift Φ depends on the wavelenght of the laser light, the mirror thickness and the indices of refraction of the mirrors and the adjacent media.

It is prefered that the recording medium according to the invention either is withgin the grooves in the high reflective area of a detuned Fabry-Perot with reflectivity higher than 70 % in the unwritten state and in the reflectance dip of a tuned Fabry-Perot with the reflectivity being below 28% of the reflectivity of the unwritten state or vice versa.

For use as a digital storage medium, it is necessary that the writing laser can be guided along a predetermined path. For this reason a substrate with a spiral shaped track, a grooved substrate, is necessary. The tracking (keeping the writing laser beam within the grooves) can take place in the digital storage medium according to the invention by employing the difference in reflected amplitude and/or phase of the thin reflective layer/substrate interface within and outside the groove resulting in diffraction. Said groove is also used for tracking with the reading laser.

As is described above, the position of the reflection dip is determined by equation 1. The width and the depth of the refelection dip is influenced by the thickness of the thin reflective layer (2) and the absorption coefficient of the liquid crystalline material layer (3). These influences can be determined with the help of a computer program based on a 2 X 2 matrix formalism for wave propagation in isotropic stratified media developed by Abelès such as described in M. Born, E. Wolf, Principles of Optics, 4 th ed., Pergamon Press (1970), p.51. The formalism by Abelès can be extended to 4 X $ matrices in order to incorporate anisotropic media (such as liquid crystalline material) as described in J. Opt. Soc. Am. 60 (1970), p. 830. It can be calculated how in digital storage medium with a substrate with refractive index n_s and a thickness d_s, a crystalline material layer with a thickness d, refractive indices n_w and n_u, and a thick reflective layer having a thickness d_m and refractive index n_m, the thickness of the thin reflective layer and/or

the absorption of the liquid crystalline material layer can be adapted to obtain a digital storage medium which is either in its written state or in its unwritten state in the reflectance dip of a tuned Fabry-Perot. These calculations are known for persons skilled in the art and need no further elucidation here.

In general, the digital storage media according to the invention will have a detuned Fabry-Perot in its unwritten state (high reflectance), and a tuned Fabry-Perot in the written areas, the pits (low reflectance), but it is also possible to start with a tuned Fabry-Perot which is locally detuned. The latter embodiment will be described later.

In the known read-only CDs the recorded information is stored in a spiral track in which regions of low reflectance (pits) are alternated by regions with the background reflectance (land) having a reflectance higher than 70 %. The pit length varies from 0.9 to 3.3 μm in 0.3 μm steps. In the longest pits (11T signal) the reflectance must drop to below 40% of the background reflectance. The readout laser in a conventional CD player has a wavelength between 780 and 830 nm, in general 780 ± 10 nm. In order to be compatible with the read-only CD, a CD according to the invention should have a reflectance in the unwritten state of 70 % and the reflectance in the longest pit should be below 40 % of the background reflectance, i.e. 28, when using a conventional readout laser for CD players.
The present invention provides for CDs having parameters which can be set to make the CD compatible with the conventional read-only CD.

The digital storage medium according to the invention comprises a grooved substrate (1). In CDs according to the invention said substrate is much thicker than the liquid crystalline layer and its mirrors (varying from 1.0 to 1.5 mm). The medium is read through the substrate. Therefore, the substrate should be optically transparent

for the laser light used for reading and writing. In conventional CD players laser light is used with a wavelength of 780 nm. Suitable substrates which are optically transparent at this wavelength and have sufficient thermal stability and resistance to humidity are polycarbonate, amorphous polyolefin, and glass. For its price and ease of handling polycarbonate substrates are preferred. However, the polycarbonate has poor resistance to solvents which are used to apply liquid crystalline material onto the substrate (provided with the thin reflective layer (2) by spin coating. Amorphous polyolefins appear to be resistant to the spin coating solvents and have equal thermal stability and resistance to humidity compared with polycarbonate. Therefore, the use of amorphous polyolefins is prefered.

In order to reduce the loss of laser light by reflection at the air substrate interface, the substrate may be provided with a anti-reflection structure on the side not covered with the thin reflective layer.

The thin reflective layer (2) is preferably a metal layer such as gold or aluminum which is applied in the substrate by, for instance, chemical vapour deposition or sputtering. The layer should be thin enough to be partially transparent for the laser light. If aluminum or gold is used, the thickness of the thin reflective layer may vary from 1 to 40 nm. The thin reflective layer is preferrably made of aluminum as this gives the highest reflection at these small thicknesses.
The thin metal layer may advantageously be used as the counter-electrode for homeotropically aligning the liquid crystalline material with poling using an electric field. In combination with the absorption coefficient of the liquid crystalline layer (3), the thickness of the thin reflective layer influences the dip in reflection in the tuned Fabry-Perot, as is explained above.

The liquid crystalline material may have a nematic, smectic, chiral smectic or cholesteric liquid crystalline phase and may be aligned uniform planair or homeotropically. It is preferred that the lquid crystalline material is homeotropically aligned in its unwritten state because in this case the refractive index of the liquid crystalline material is independent of the polarisation of the incident light.

Homeotropic orientation of the liquid-crystalline material can be attained in several ways:

1. By treating the surface of the substrate with homeotropic orientation inducing surfactants. These may be, int. al., silanes, higher alcohols, and the like, e.g., n-dodecanol and Liquicoat® PA, ex Merck.
2. By poling the liquid-crystalline layer in a magnetic or electric field. The electric field may be generated by corona poling (using a sharp needle, sharp knife or a thin wire as electrode). There will have to be a counter-electrode on the other side of the liquid-crystalline layer (e.g., an ITO-layer, a metal layer, or a conductive polymer layer), so that the poling field will be positioned over the liquid-crystalline layer. Alternatively, the liquid-crystalline layer may be provided with a conductive layer on either side, and an electric field applied thereto.

Uniform planar orientation can likewise be obtained by surface treatment, or by shear.

Suitable liquid crystalline materials which may be used for layer (3) is high molecular weight material (1000-250 000) such as liquid crystalline polymers and liquid crystalline glasses. From the liquid crystalline polymers side chain polyesters, side chain polyurethanes, and side chain polyethers are prefered, for their polability, their thermal stability (Tg), and suitable viscosity. For further information on liquid crystalline side-chain polyesters reference may

be had in EP-A1-0 478 052 which is incorporated herein by reference. Information on liquid crystalline side-chain polyurethanes may be obtained from EP-A1-0 350 112 which is also incorporated by reference. For information on liquid crystalline side-chain polyethers reference may be had in International application No. PCT/EP 95/03176.

Liquid crystalline glasses are also very suitable for use in digital storage media according to the invention as they are thermally stable, readily polable, and have a low viscosity above Tg. For information on liquid crystalline glasses reference may be had in Ineternational patent application No. PCT/EP 95/02981.

The absorption coefficient of the liquid crystalline material layer can be set by incorporating dyes in the liquid crystalline material. The absorption coefficient of the liquid crystalline material layer is determined by the absorption of the liquid crystalline material (which is normaly neglectible in the wavelenght area of 750-800 nm), the extinction coefficient of the dye used and the concentration of the dye. As is mentioned above, the absorption coefficent of the liquid crystalline material in combination with the thickness of the thin reflective layer (2) influences the depth and width of the dip in reflectivity. In genereal up to 30 wt% dye may be present in the liquid-crystalline material.

As mentioned-above the Fabry-Perot phenomenon can also be used to enhance the contrast between written and unwritten parts on the digital storage medium of media in which the contrast is based on difference in media based on pit-edge interference. If a digital storage medium is prepared containing a liquid crystalline layer which comprises a dichroic dye, it is possible to read the information via the difference in absorption, which results in a difference in reflection. Said difference in reflection may be enhanced by using a digital storage medium according to the invention having two

reflective layers, with for instance a high reflectivity in the unwritten state and a low refelctivity in the written state owing to the Fabrý-Perot phemonenon.
The digital storage media according to the invention having homeotropically alligned liquid crystalline material which comprises a dichroic dye are prefered, because these CDs have a higher contrast than the CDs based on pit-edge interference. In fact, in CDs with homeotropically alligned liquid crystalline material and dichroic dye both phenomena are active simultaneously, and it is impossible to tell the contribution of each phenomenon to the contrast. For further information on digital storage media with homeotropical alignment and dichroic dyes, reference may be had in EP-A1-0 608 924, and International application No. PCT/EP 95/03176 (LC polyethers) and International patent application No. PCT/EP 95/02981 (LC glasses).

As mentioned above, the absorption coefficient in combination with the thickness of the thin reflective layer influences the dip in reflectivity in the tuned Fabry-Perot. The absorption coefficient is determined by the dye concentration and its extinction coefficient in the liquid crystalline layer. This can be used to determine the paramaters for CDs according to the invention which are compatible with the conventional read-only CDs.

The thick reflective layer is preferrably a metal layer such as gold or aluminum which is applied in the liquid crystalline layer by, for instance chemical vapour deposition or sputtering. This thick layer should not be transparant for the laser light and therefore should have a thickness of at least 40 nm. As aluminum is cheaper than gold, and the reflectivity of an aluminum layer with a thickness above 70 nm is as sufficiently high, the use of aluminum for the thick reflective layer is prefered.

In another embodiment of the digital storage medium according to the invention the liquid crystalline material fulfills the requirements of constructive interference for a Fabry-perot etalon in its unwritten state. As mentioned above, the substrate contains a spiral track (groove) to allow radial tracking of the laser focus during writing. It is possible to make a CD wherein the Fabry-Perot is tuned within the groove (low reflectivity) and detuned in the land (high reflectivity), because there is a difference in thickness of the liquid crystalline layer within the groove and in the land. The pits which are written in the groove should remain to have said low reflectivity (the Fabry-Perot should remain tuned), whereas the rest of the groove writing should obtain the same high reflectivity as the land. This can easily be done by irradiating, and thus detuning the Fabry-Perot, in the areas in the groove outside the pits. This is illustrated in figure 2, wherein a CD according to the invention comprises a substrate (1), a thin reflective layer (2), a liquid crystalline material layer (3) which is provided with a groove (6), and a thick reflective layer (4) is depicted. Said CD is irradiated with laser beam (5).

Claims

1. A digital storage medium comprising:
a grooved substrate (1) provided with a thin reflective layer (2) being partially transparant, which is provided with a layer (3), which comprises liquid crystalline material having a thickness (d) between 100 and 1200 nm, which is provided with a thick reflective layer (4) having a reflectance above 50%.

2. A digital storage medium according to claim 1, wherein the reflection of the medium within the grooves is in the high reflective area of a detuned Fabry-Perot with reflectivity higher than 70 % in the unwritten state and in the reflectance dip of a tuned Fabry-Perot with the reflectivity being below 28% of the reflectivity of the unwritten state, or vice versa.

3. A digital storage medium according to claim 1 or 2, wherein the grooved substrate (1) is provided with an anti-reflection structure on the side not covered with the thin reflective layer.

4. A digital storage medium according to claim 1,2 or 3, wherein the grooved substate (1) is an amorphous polyolefin.

5. A digital storage medium according to any of the preceding claims, wherein the thin reflective layer (2) is a metal layer such as gold.

6. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material comprises a dye.

7. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material is homeotropically aligned in its unwritten state.

8. A digital storage medium according to claim 7, wherein the liquid crystalline material comprises a dichroic dye.

9. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material comprises a liquid crystalline polymer.

10. A digital storage medium according to claim 9, wherein the liquid crystalline polymer is a LC side-chain polyester, polyurethane or polyether.

11. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material comprises a liquid crystalline glass.

12. A digital storage medium according to any of the preceding claims, wherein the thick reflective layer is a metal layer.

13. A digital storage medium according to any of the preceding claims, wherein the thick reflective layer is an gold layer.

14. A digital storage medium according to any of the preceding claims, wherein the thick reflective layer is an aluminum layer.

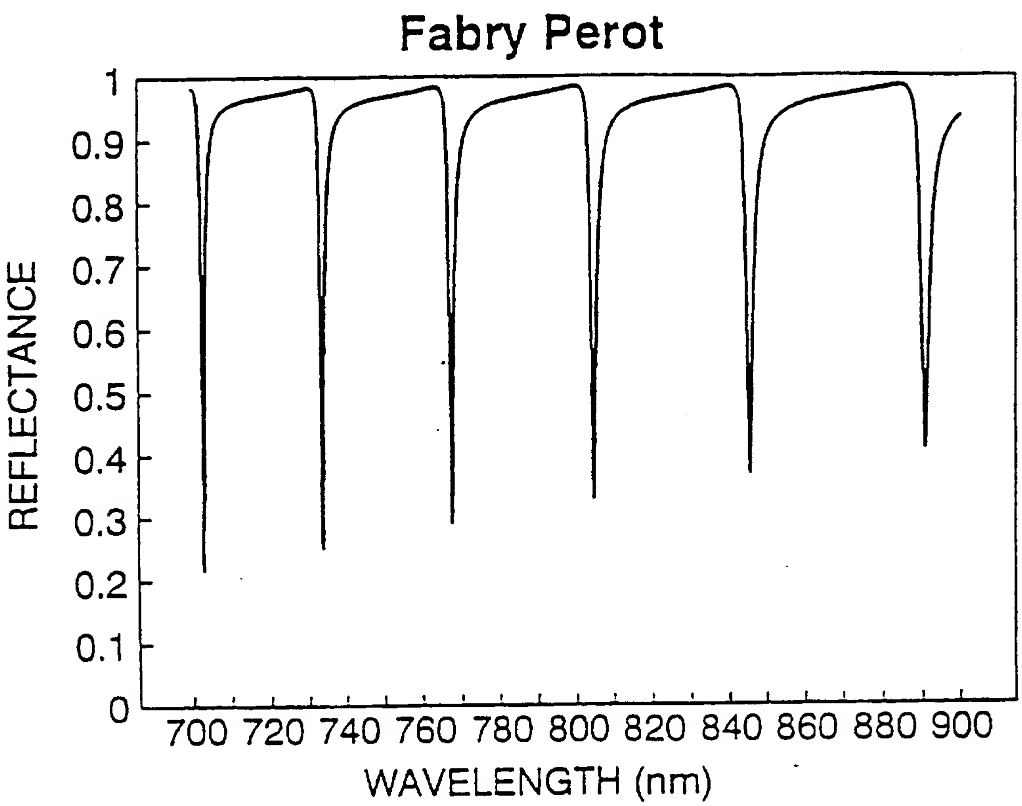
15. A digital storage medium according to any of the preceding claims, wherein in the groove the liquid crystalline material fulfills the requirements of constructive interference for a Fabry-perot etalon in its unwritten state.

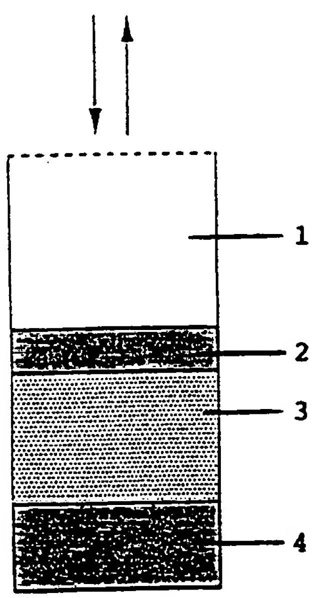
16. A digital storage medium according to any of the preceding claims, wherein the digital storage medium is a compact disc.

17. A digital storage medium according to any of the preceding claims, wherein the digital storage medium is a digital card or tape.

18. Method for the preparation of the digital storage medium according to any of the preceding claims 1-16, wherein the thickness of the thin reflective layer (2) and the absorption coefficient of the liquid crystalline material layer(3) is set to make refelection of the medium in the reflection dip of a tuned Fabry-Perot either in the written state or in the unwritten state.

Figure 1


Fabry Perot
REFLECTANCE
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
700 720 740 760 780 800 820 840 860 880 900
WAVELENGTH (nm)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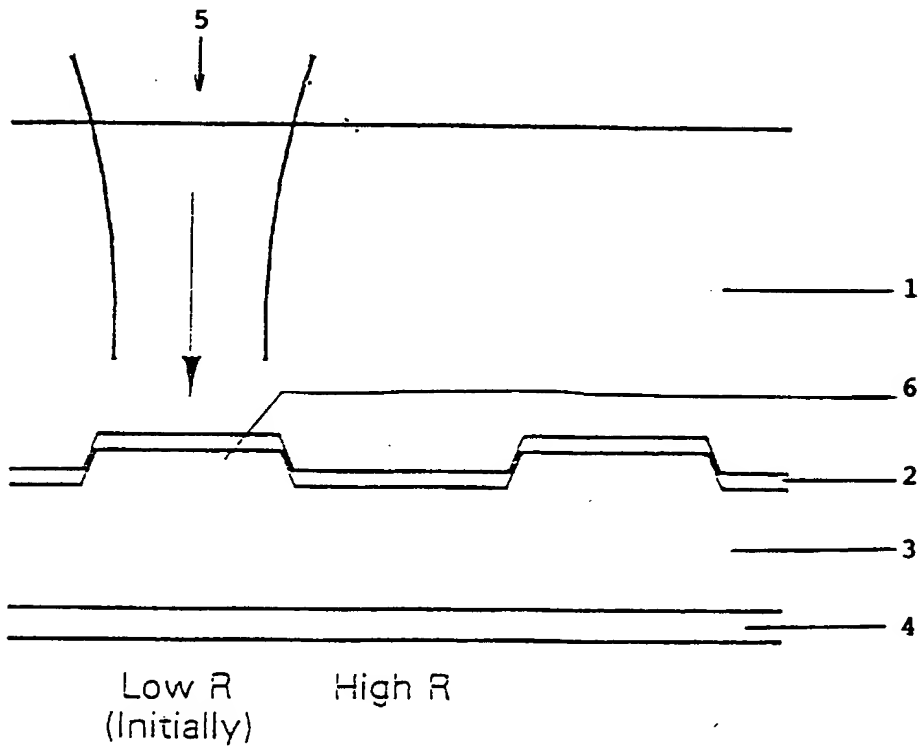
2 / 2

Figure 2



INTERNATIONAL SEARCH REPORT

Inter nal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 015 no. 162 (P-1194) ,23 April 1991 & JP,A,03 029117 (CANON INC) 7 February 1991, see abstract ---	1,9
Y	EP,A,0 271 900 (CANON KK) 22 June 1988 see page 9, line 57 - page 11, line 47; figure 14 ---	1,5-18
Y	EP,A,0 461 619 (CANON KK) 18 December 1991 see the whole document ---	1,5-18
A	EP,A,0 278 446 (BASF AG) 17 August 1988 see the whole document ---	1,5-12, 14,16-18

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 235 748 (SEMICONDUCTOR ENERGY LAB) 9 September 1987 see column 2; figure 2 -----	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/EP 95/04605

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0271900	22-06-88	JP-A-	1013117	18-01-89
		JP-A-	63153520	25-06-88
		DE-D-	3788634	10-02-94
		DE-T-	3788634	19-05-94
		EP-A-	0528449	24-02-93
		US-A-	4995705	26-02-91
		JP-A-	63271228	09-11-88
		JP-A-	63266647	02-11-88
EP-A-0461619	18-12-91	JP-A-	4228132	18-08-92
		US-A-	5316806	31-05-94
EP-A-0278446	17-08-88	DE-A-	3704146	29-09-88
		DE-D-	3884420	04-11-93
		JP-A-	63216791	09-09-88
		US-A-	5097463	17-03-92
EP-A-0235748	09-09-87	JP-A-	62204486	09-09-87
		JP-A-	62204445	09-09-87
		JP-A-	62205551	10-09-87
		JP-C-	1794506	14-10-93
		JP-B-	4081814	25-12-92
		JP-A-	63031037	09-02-88
		US-A-	4832456	23-05-89

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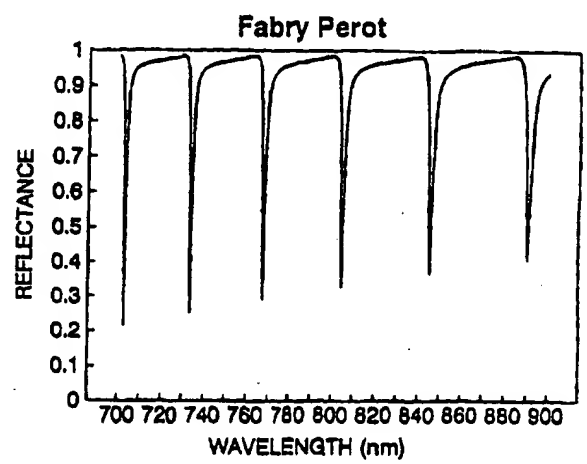
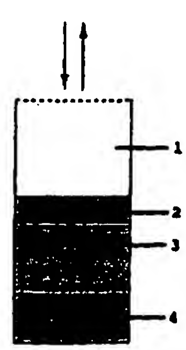
(54) Title: DIGITAL STORAGE MEDIUM BASED ON FABRY-PEROT PRINCIPLE

(57) Abstract

The present invention is in the field of digital storage media, more particularly on so-called WORM media (write-once-read-many-times compact discs) and rewritable media. The digital storage medium according to the invention comprises a grooved substrate (1) provided with a thin reflective layer (2) being partially transparent, which is provided with a layer (3), which comprises liquid crystalline material having a thickness (d) between 100 and 1200 nm, which is provided with a thick reflective layer (4) having a reflectance above 50 %. When using a CD according to this invention, the Fabry-Perot phenomenon is used to obtain or enhance a difference in reflection between the written and unwritten state.





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DIGITAL STORAGE MEDIUM BASED ON FABRY-PEROT PRINCIPLE

The present invention is in the field of digital storage media, such as compact discs (CDs) and digital tapes or cards, more particularly on so-called WORM media (write-once-read-many-times compact discs or tapes) and rewritable CDs and tapes. These types of media allow the information being written by the consumer.

In conventional read-only CDs the information is stored in pits which are embossed in the disc. The reading is based on pit-edge interference: As the laser focus is wider than the pit (0.6 μm), interference occurs between the laser light which falls within the pit and laser light which falls outside the pit (land). This results in a modulation in reflection, which is used for reading the information.
The conventional read-only CDs are only suitable for large production, as the production steps (for obtaining a written disc) are rather complicated and therefore only cost effective in mass production. There is a need for CDs and digital tapes or cards which can be produced in small quantities, or which can even be written by the consumer himself. One of the proposed concepts for this kind of WORM or rewritable CD is a CD comprising a liquid crystalline polymer (LCP) layer which is coated on a reflective layer. The writing is done by locally changing the phase of the LCP by means of laser irradiation. This results in a change of refractive index in the pit. The reading is again based on pit-edge interference: When irradiating with the reading laser the light travels through the LCP layer and reflects at the reflective layer. As the refractive index within a pit differs from the refractive index outside the pit (land), the optical pathlenght within the pit differs from that of the land. The laser light which falls within the the pit interferes with the light which falls on the land. The resulting reflection modulation is used for reading the information. This kind of CD is described in, for instance, CA-A1-2,014,698.

In EP-A1-0 608 924 a storage medium is described which comprises a homeotropically aligned LCP layer having a dichroic dye dispersed therein. The reading principle is now based on difference in absorption: In the homeotropic phase the dichroic dye is alligned along with the mesogenic groups of the LCP, which is perpendicular to the surface of the medium. In this state there is only low absorption of the incident light by the dichroic dye molecules, thus a high reflectance. After local irradiation of the LCP, the mesogenic groups, and thus the dye molecules, are orientated randomly, which results in a higher absorption of the incident light by the dye molecules, thus a lower reflectance.

There is still need of improvement in reflectivity and contrast in the WORM media and rewritable media proposed sofar.
The present invention provides a digital medium having an enhanced change in reflection.

The digital storage medium according to the invention comprises a grooved substrate (1) provided with a thin reflective layer (2) being partially transparant, which is provided with a layer (3), which comprises liquid crystalline material having a thickness (d) between 100 and 1200 nm, which is provided with a thick reflective layer (4) having a reflectance above 50%.

Thus, in comparison with the known digital storage media, an extra thin reflective layer is present, resulting in the liquid crystalline material layer (3) being sandwiched between two reflective layers. Herewith a Fabry-Perot etalon is created. The Fabry-Perot phenomenon is used to obtain a difference in reflection between the written and unwritten state in the digital storage medium. The difference in reflection between the written and unwritten areas in digital media based on difference in absorption and digital media based on pit-edge interference may also be enhanced by introducing the Fabry-Perot

phenomenon. A Fabry-Perot etalon typically consists of two parallel, reflecting layers that are placed at some distance (d) from each other. The dependence of the reflectance of a Fabry-Perot etalon on the wavelength is shown in figure 1, wherein schematically a CD is depicted with a substrate (1) having a refractive index of 1.58 and a thickness of 1.2 mm, a thin reflective layer (2) having a refractive index of 0.08 + i 4.60 and a thickness of 30 nm, a liquid crystallina material layer (3) having a refractive index of 1.67 and a thickness of 5 μm, and a thick reflective layer (4) having a refractive index of 0.08 + i 4.60 and a thickness of 200 nm. In general, the reflectance is high. At regular intervals, however, the reflectance changes abruptly to a low value. This negative peak in reflectance is hereinafter referred to as reflection dip. This resonance-like behaviour occurs when light cycling back and forth between mirrors interferes constructively with itself. This is the case when the requirements of equation 1 are fulfilled. If the requirements of equation 1 are fulfilled the reflectance is low.

$$\Phi + (4\pi \times n \times d)/\lambda = m \times 2\pi \qquad \text{[equation 1]}$$

wherein

- Φ stands for the phase shift of the laser light on reflection by the mirrors,
- n stands for either n_u or n_w,
- d stands for the layer thickness of the liquid crystalline material,
- λ stands for the wavelength of the laser light used for reading,
- m is an integer from 1-5.

The phase shift Φ depends on the wavelenght of the laser light, the mirror thickness and the indices of refraction of the mirrors and the adjacent media.

It is prefered that the recording medium according to the invention either is withgin the grooves in the high reflective area of a detuned Fabry-Perot with reflectivity higher than 70 % in the unwritten state and in the reflectance dip of a tuned Fabry-Perot with the reflectivity being below 28% of the reflectivity of the unwritten state or vice versa.

For use as a digital storage medium, it is necessary that the writing laser can be guided along a predetermined path. For this reason a substrate with a spiral shaped track, a grooved substrate, is necessary. The tracking (keeping the writing laser beam within the grooves) can take place in the digital storage medium according to the invention by employing the difference in reflected amplitude and/or phase of the thin reflective layer/substrate interface within and outside the groove resulting in diffraction. Said groove is also used for tracking with the reading laser.

As is described above, the position of the reflection dip is determined by equation 1. The width and the depth of the refelection dip is influenced by the thickness of the thin reflective layer (2) and the absorption coefficient of the liquid crystalline material layer (3). These influences can be determined with the help of a computer program based on a 2 X 2 matrix formalism for wave propagation in isotropic stratified media developed by Abelès such as described in M. Born, E. Wolf, Principles of Optics, 4 th ed., Pergamon Press (1970), p.51. The formalism by Abelès can be extended to 4 X $ matrices in order to incorporate anisotropic media (such as liquid crystalline material) as described in J. Opt. Soc. Am. 60 (1970), p. 830. It can be calculated how in digital storage medium with a substrate with refractive index n_s and a thickness d_s, a crystalline material layer with a thickness d, refractive indices n_w and n_u, and a thick reflective layer having a thickness d_m and refractive index n_m, the thickness of the thin reflective layer and/or

the absorption of the liquid crystalline material layer can be adapted to obtain a digital storage medium which is either in its written state or in its unwritten state in the reflectance dip of a tuned Fabry-Perot. These calculations are known for persons skilled in the art and need no further elucidation here.

In general, the digital storage media according to the invention will have a detuned Fabry-Perot in its unwritten state (high reflectance), and a tuned Fabry-Perot in the written areas, the pits (low reflectance), but it is also possible to start with a tuned Fabry-Perot which is locally detuned. The latter embodiment will be described later.

In the known read-only CDs the recorded information is stored in a spiral track in which regions of low reflectance (pits) are alternated by regions with the background reflectance (land) having a reflectance higher than 70 %. The pit length varies from 0.9 to 3.3 μm in 0.3 μm steps. In the longest pits (11T signal) the reflectance must drop to below 40% of the background reflectance. The readout laser in a conventional CD player has a wavelength between 780 and 830 nm, in general 780 ± 10 nm. In order to be compatible with the read-only CD, a CD according to the invention should have a reflectance in the unwritten state of 70 % and the reflectance in the longest pit should be below 40 % of the background reflectance, i.e. 28, when using a conventional readout laser for CD players.
The present invention provides for CDs having parameters which can be set to make the CD compatible with the conventional read-only CD.

The digital storage medium according to the invention comprises a grooved substrate (1). In CDs according to the invention said substrate is much thicker than the liquid crystalline layer and its mirrors (varying from 1.0 to 1.5 mm). The medium is read through the substrate. Therefore, the substrate should be optically transparent

for the laser light used for reading and writing. In conventional CD players laser light is used with a wavelength of 780 nm. Suitable substrates which are optically transparent at this wavelength and have sufficient thermal stability and resistance to humidity are polycarbonate, amorphous polyolefin, and glass. For its price and ease of handling polycarbonate substrates are preferred. However, the polycarbonate has poor resistance to solvents which are used to apply liquid crystalline material onto the substrate (provided with the thin reflective layer (2) by spin coating. Amorphous polyolefins appear to be resistant to the spin coating solvents and have equal thermal stability and resistance to humidity compared with polycarbonate. Therefore, the use of amorphous polyolefins is prefered.

In order to reduce the loss of laser light by reflection at the air substrate interface, the substrate may be provided with a anti-reflection structure on the side not covered with the thin reflective layer.

The thin reflective layer (2) is preferably a metal layer such as gold or aluminum which is applied in the substrate by, for instance, chemical vapour deposition or sputtering. The layer should be thin enough to be partially transparent for the laser light. If aluminum or gold is used, the thickness of the thin reflective layer may vary from 1 to 40 nm. The thin reflective layer is preferrably made of aluminum as this gives the highest reflection at these small thicknesses.
The thin metal layer may advantageously be used as the counter-electrode for homeotropically aligning the liquid crystalline material with poling using an electric field. In combination with the absorption coefficient of the liquid crystalline layer (3), the thickness of the thin reflective layer influences the dip in reflection in the tuned Fabry-Perot, as is explained above.

The liquid crystalline material may have a nematic, smectic, chiral smectic or cholesteric liquid crystalline phase and may be aligned uniform planair or homeotropically. It is preferred that the lquid crystalline material is homeotropically aligned in its unwritten state because in this case the refractive index of the liquid crystalline material is independent of the polarisation of the incident light.

Homeotropic orientation of the liquid-crystalline material can be attained in several ways:

1. By treating the surface of the substrate with homeotropic orientation inducing surfactants. These may be, int. al., silanes, higher alcohols, and the like, e.g., n-dodecanol and Liquicoat® PA, ex Merck.
2. By poling the liquid-crystalline layer in a magnetic or electric field. The electric field may be generated by corona poling (using a sharp needle, sharp knife or a thin wire as electrode). There will have to be a counter-electrode on the other side of the liquid-crystalline layer (e.g., an ITO-layer, a metal layer, or a conductive polymer layer), so that the poling field will be positioned over the liquid-crystalline layer. Alternatively, the liquid-crystalline layer may be provided with a conductive layer on either side, and an electric field applied thereto.

Uniform planar orientation can likewise be obtained by surface treatment, or by shear.

Suitable liquid crystalline materials which may be used for layer (3) is high molecular weight material (1000-250 000) such as liquid crystalline polymers and liquid crystalline glasses. From the liquid crystalline polymers side chain polyesters, side chain polyurethanes, and side chain polyethers are prefered, for their polability, their thermal stability (Tg), and suitable viscosity. For further information on liquid crystalline side-chain polyesters reference may

be had in EP-A1-0 478 052 which is incorporated herein by reference. Information on liquid crystalline side-chain polyurethanes may be obtained from EP-A1-0 350 112 which is also incorporated by reference. For information on liquid crystalline side-chain polyethers reference may be had in International application No. PCT/EP 95/03176.

Liquid crystalline glasses are also very suitable for use in digital storage media according to the invention as they are thermally stable, readily polable, and have a low viscosity above Tg. For information on liquid crystalline glasses reference may be had in Ineternational patent application No. PCT/EP 95/02981.

The absorption coefficient of the liquid crystalline material layer can be set by incorporating dyes in the liquid crystalline material. The absorption coefficient of the liquid crystalline material layer is determined by the absorption of the liquid crystalline material (which is normaly neglectible in the wavelenght area of 750-800 nm), the extinction coefficient of the dye used and the concentration of the dye. As is mentioned above, the absorption coefficent of the liquid crystalline material in combination with the thickness of the thin reflective layer (2) influences the depth and width of the dip in reflectivity. In genereal up to 30 wt% dye may be present in the liquid-crystalline material.

As mentioned-above the Fabry-Perot phenomenon can also be used to enhance the contrast between written and unwritten parts on the digital storage medium of media in which the contrast is based on difference in media based on pit-edge interference. If a digital storage medium is prepared containing a liquid crystalline layer which comprises a dichroic dye, it is possible to read the information via the difference in absorption, which results in a difference in reflection. Said difference in reflection may be enhanced by using a digital storage medium according to the invention having two

reflective layers, with for instance a high reflectivity in the unwritten state and a low refelctivity in the written state owing to the Fabry-Perot phemonenon.

The digital storage media according to the invention having homeotropically alligned liquid crystalline material which comprises a dichroic dye are prefered, because these CDs have a higher contrast than the CDs based on pit-edge interference. In fact, in CDs with homeotropically alligned liquid crystalline material and dichroic dye both phenomena are active simultaneously, and it is impossible to tell the contribution of each phenomenon to the contrast. For further information on digital storage media with homeotropical alignment and dichroic dyes, reference may be had in EP-A1-0 608 924, and International application No. PCT/EP 95/03176 (LC polyethers) and International patent application No. PCT/EP 95/02981 (LC glasses).

As mentioned above, the absorption coefficient in combination with the thickness of the thin reflective layer influences the dip in reflectivity in the tuned Fabry-Perot. The absorption coefficient is determined by the dye concentration and its extinction coefficient in the liquid crystalline layer. This can be used to determine the paramaters for CDs according to the invention which are compatible with the conventional read-only CDs.

The thick reflective layer is preferrably a metal layer such as gold or aluminum which is applied in the liquid crystalline layer by, for instance chemical vapour deposition or sputtering. This thick layer should not be transparant for the laser light and therefore should have a thickness of at least 40 nm. As aluminum is cheaper than gold, and the reflectivity of an aluminum layer with a thickness above 70 nm is as sufficiently high, the use of aluminum for the thick reflective layer is prefered.

In another embodiment of the digital storage medium according to the invention the liquid crystalline material fulfills the requirements of constructive interference for a Fabry-perot etalon in its unwritten state. As mentioned above, the substrate contains a spiral track (groove) to allow radial tracking of the laser focus during writing. It is possible to make a CD wherein the Fabry-Perot is tuned within the groove (low reflectivity) and detuned in the land (high reflectivity), because there is a difference in thickness of the liquid crystalline layer within the groove and in the land. The pits which are written in the groove should remain to have said low reflectivity (the Fabry-Perot should remain tuned), whereas the rest of the groove writing should obtain the same high reflectivity as the land. This can easily be done by irradiating, and thus detuning the Fabry-Perot, in the areas in the groove outside the pits. This is illustrated in figure 2, wherein a CD according to the invention comprises a substrate (1), a thin reflective layer (2), a liquid crystalline material layer (3) which is provided with a groove (6), and a thick reflective layer (4) is depicted. Said CD is irradiated with laser beam (5).

Claims

1. A digital storage medium comprising:
a grooved substrate (1) provided with a thin reflective layer (2) being partially transparant, which is provided with a layer (3), which comprises liquid crystalline material having a thickness (d) between 100 and 1200 nm, which is provided with a thick reflective layer (4) having a reflectance above 50%.

2. A digital storage medium according to claim 1, wherein the reflection of the medium within the grooves is in the high reflective area of a detuned Fabry-Perot with reflectivity higher than 70 % in the unwritten state and in the reflectance dip of a tuned Fabry-Perot with the reflectivity being below 28% of the reflectivity of the unwritten state, or vice versa.

3. A digital storage medium according to claim 1 or 2, wherein the grooved substrate (1) is provided with an anti-reflection structure on the side not covered with the thin reflective layer.

4. A digital storage medium according to claim 1,2 or 3, wherein the grooved substate (1) is an amorphous polyolefin.

5. A digital storage medium according to any of the preceding claims, wherein the thin reflective layer (2) is a metal layer such as gold.

6. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material comprises a dye.

7. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material is homeotropically aligned in its unwritten state.

8. A digital storage medium according to claim 7, wherein the liquid crystalline material comprises a dichroic dye.

9. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material comprises a liquid crystalline polymer.

10. A digital storage medium according to claim 9, wherein the liquid crystalline polymer is a LC side-chain polyester, polyurethane or polyether.

11. A digital storage medium according to any of the preceding claims, wherein the liquid crystalline material comprises a liquid crystalline glass.

12. A digital storage medium according to any of the preceding claims, wherein the thick reflective layer is a metal layer.

13. A digital storage medium according to any of the preceding claims, wherein the thick reflective layer is an gold layer.

14. A digital storage medium according to any of the preceding claims, wherein the thick reflective layer is an aluminum layer.

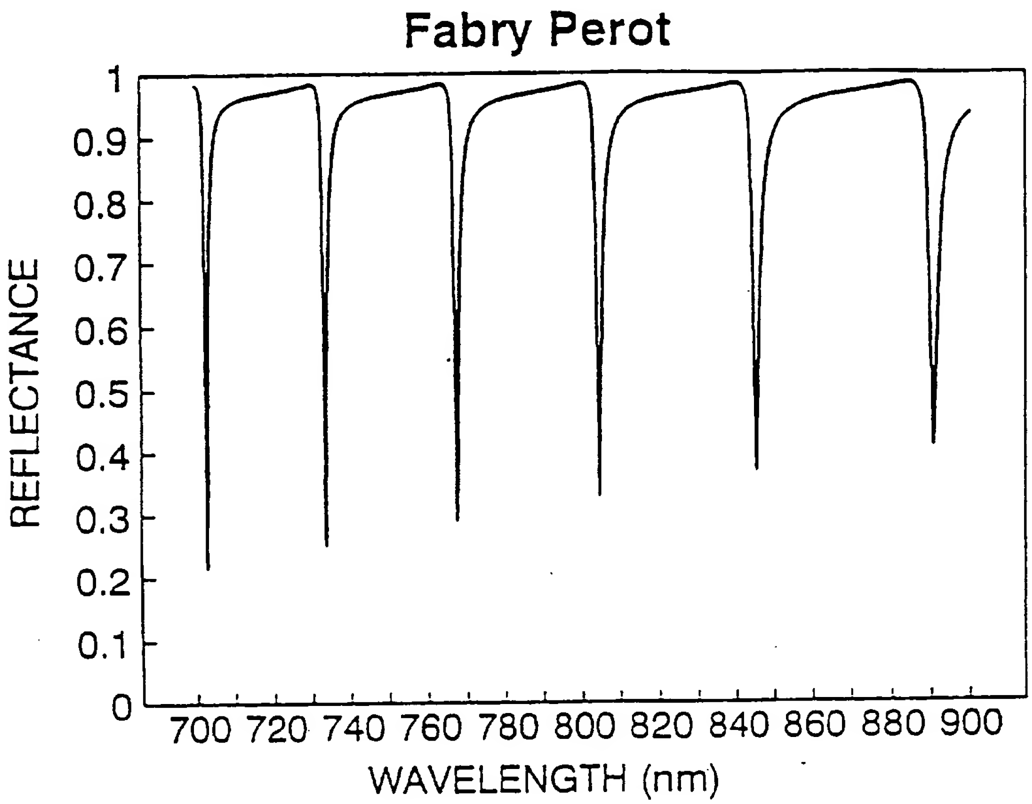
15. A digital storage medium according to any of the preceding claims, wherein in the groove the liquid crystalline material fulfills the requirements of constructive interference for a Fabry-perot etalon in its unwritten state.

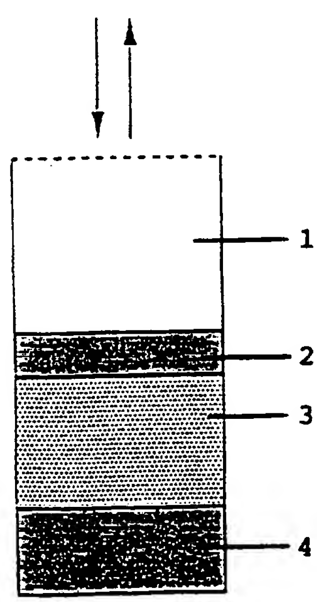
16. A digital storage medium according to any of the preceding claims, wherein the digital storage medium is a compact disc.

17. A digital storage medium according to any of the preceding claims, wherein the digital storage medium is a digital card or tape.

18. Method for the preparation of the digital storage medium according to any of the preceding claims 1-16, wherein the thickness of the thin reflective layer (2) and the absorption coefficient of the liquid crystalline material layer(3) is set to make refelection of the medium in the reflection dip of a tuned Fabry-Perot either in the written state or in the unwritten state.

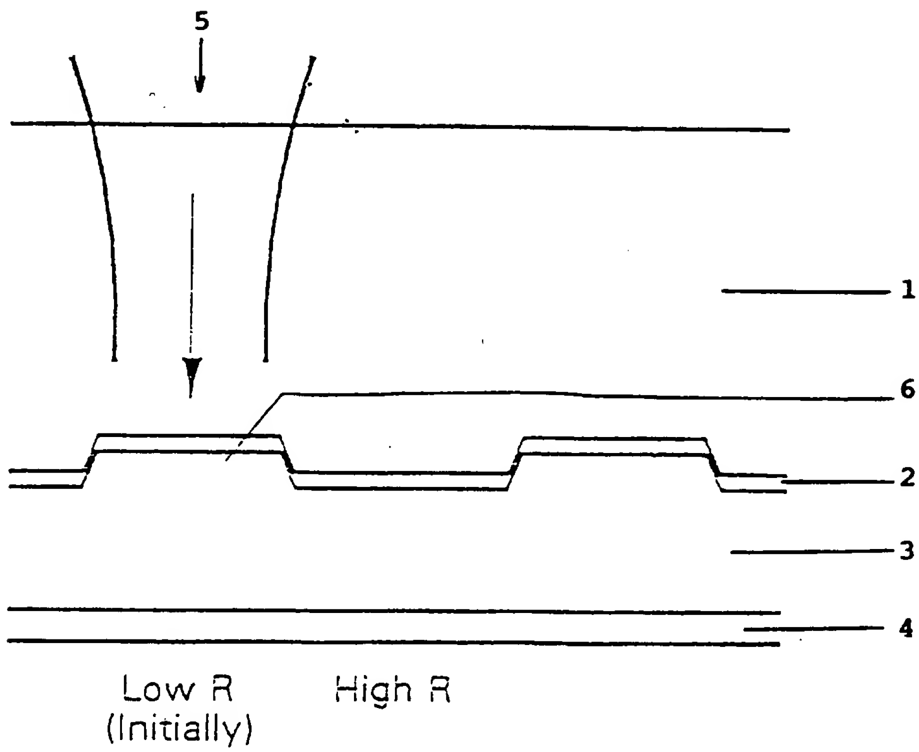
Figure 1


Fabry Perot
REFLECTANCE
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
700 720 740 760 780 800 820 840 860 880 900
WAVELENGTH (nm)


1
2
3
4

2 / 2

Figure 2



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/04605

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 015 no. 162 (P-1194) ,23 April 1991 & JP,A,03 029117 (CANON INC) 7 February 1991, see abstract ---	1,9
Y	EP,A,0 271 900 (CANON KK) 22 June 1988 see page 9, line 57 - page 11, line 47; figure 14 ---	1,5-18
Y	EP,A,0 461 619 (CANON KK) 18 December 1991 see the whole document ---	1,5-18
A	EP,A,0 278 446 (BASF AG) 17 August 1988 see the whole document ---	1,5-12, 14,16-18

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 95/04605

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 235 748 (SEMICONDUCTOR ENERGY LAB) 9 September 1987 see column 2; figure 2 -----	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 95/04605

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0271900	22-06-88	JP-A- 1013117	18-01-89
		JP-A- 63153520	25-06-88
		DE-D- 3788634	10-02-94
		DE-T- 3788634	19-05-94
		EP-A- 0528449	24-02-93
		US-A- 4995705	26-02-91
		JP-A- 63271228	09-11-88
		JP-A- 63266647	02-11-88
EP-A-0461619	18-12-91	JP-A- 4228132	18-08-92
		US-A- 5316806	31-05-94
EP-A-0278446	17-08-88	DE-A- 3704146	29-09-88
		DE-D- 3884420	04-11-93
		JP-A- 63216791	09-09-88
		US-A- 5097463	17-03-92
EP-A-0235748	09-09-87	JP-A- 62204486	09-09-87
		JP-A- 62204445	09-09-87
		JP-A- 62205551	10-09-87
		JP-C- 1794506	14-10-93
		JP-B- 4081814	25-12-92
		JP-A- 63031037	09-02-88
		US-A- 4832456	23-05-89